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Measuring the Specific Heat of Magnetic Fluids using a Differential Scanning Calorimeter¹

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ABSTRACT

The specific heat of magnetic fluids is measured using a heat flux type differential scanning calorimeter (DSC). Magnetic fluids which contain 10-43 wt % ultrafine magnetite (Fe $_3$ O $_4$) particles dispersed with surfactants in water or kerosene are used. DSC was operated with the optimum heating rate ($10\text{K} \cdot \text{m}^{-1}$) and the equal heat capacities of sample and standard materials in the temperature range 295 to 345 K. Synthetic sapphire (α -Al $_2$ O $_3$) as the standard reference material and sample pan made of aluminum are used. The differences between the obtained specific heat values of pure water and pure copper and the recommended values are within \pm 3% and \pm 1%, respectively. The specific heat data of magnetic fluids are show weak temperature-dependence, but strong concentration-dependence. The measured values of specific heat of magnetic fluids are compared with the calculated values from the mixing rule of mixtures.

KEY WORDS: concentration-dependency; differential scanning calorimeter; magnetic fluids; magnetite; mixing rule; mixtures; specific heat; temperature-dependency

1. INTRODUCTION

A magnetic fluid consists typically of a stable colloidal suspension of monodomain ferromagnetic particles such as magnetite (Fe₃O₄, size smaller than 100 Å=100×10⁻¹⁰ m) in a nonmagnetic carrier fluid. A surfactant covering the particles prevents particle-to-particle agglomeration, and Brownian motion prevents particle sedimentation in gravitational or magnetic fields [1-4]. Magnetic fluids are used extensively in devices such as high-speed rotating shaft seals, inertia dampers and as a coolant of heat exchange devices [5]. Recently, thermal environments used these devices become severe, the data of thermophysical properties of magnetic fluids are required for the thermal design of devices. While many books and papers have been published [1-6] which include informations on the structure and properties of magnetic fluids, the thermophysical properties of magnetic fluids for evaluating heat transfer are not always found in books and papers.

The specific heat of magnetic fluids is one of the important thermophysical properties for evaluating heat transfer in devices. It needs to clarify its dependencies on temperature and ferromagnetic particles concentration. Venger et al. [7] reported the temperature-dependence of the specific heat of magnetic fluids in the range 320 to 373 K without magnetic fields, and presented the equation for calculating the specific heat of magnetic fluids by "the mixing rule"[5,6]. To the author's knowledge, there is no paper reported about the specific heat of magnetic fluids without Venger et al. [7].

The purpose of this paper is to measure the specific heats of water-based and kerosene-based magnetic fluids using differential scanning calorimeter (abbreviation; DSC) and to clarify its dependencies on temperature and magnetite concentration. Copper, distilled water and synthetic sapphire as standard reference materials of specific heat are also measured to determine the optimum procedure, and to check the reliability of the DSC.

2. MEASUREMENTS

2.1 Magnetic Fluids

Two Magnetic fluids contained magnetite (Fe₃O₄) as ferromagnetic particles are Marpo Magna FW-40 (magnetite,42.0; surfactant, 14.7; water as a base liquid,43.3 wt %) and the other is Marpo Magna FN-40 (magnetite,43.0; surfactant, 11.7; kerosene as a base liquid, 45.3 wt %) as reported in the technical bulletin of MATSUMOTO YUSHI-SEIYAKU Co., Ltd.. Both magnetic fluids are diluted by adding only a base liquid. Since surfactant used is not shown in the technical bulletin, oleic acid as a surfactant is assumed as same as the literatures[6,7].

2.2 Apparatus

A heat-flux type differential scanning calorimeter (RIGAKU-DENNKI Co., Ltd., Thermal Analysis System 200 with Model 8230-D module) is used for measuring the specific heat of magnetic fluids. Maximum heating rate of his DSC is 20 K•min⁻¹ (0.33 K•s⁻¹). Synthetic sapphire (α -Al₂O₃) supplied by manufacturer is used as a standard reference material. Sample pans are made of aluminum. Crimped pans for a reference material and solid samples, and sealed pans for liquid samples are used for measurements. METLLER AE163 submicrobalance (resolution,± 0.01mg) is used to weigh the all pans and the empty pans. The mass differences of a set of any types of pans used for measurements are within ± 0.02 mg.

2.3 Procedure

Detail description of procedure for using the DSC is in the literature[8,9]. DSC for the heat capacity measurement was initially calibrated for temperature and calorimetric sensitivity. Temperature calibration was accomplished using the melting points of Indium, Tin and Lead, and the calorimetric sensitivity was determined using the enthalpy of fusion of these materials. Results of the temperature calibration at a heating rate 10 K•min⁻¹ were better than that at 1 K•min⁻¹. Heat-flux type DSC have reverse behavior to power-compensated type DSC [10]. DSC was scanned with the

optimum heating rate for a span of 70 K. The specific heat of pure copper was measured with various heating rates, and the optimum heating rate for accurate measurement was determined. Distilled water, synthetic sapphire used as a standard reference material was also measured to check the reliability of DSC. DSC was scanned under the condition tof hat the heat capacity (specific heat times mass) of sample is equal with that of standard material. For accurate measurement s, the sample mass was carefully determined. The output signals of DSC was processed with cosideration of the time lag of sample temperature to gain the isothermal base line in the DSC curves. These procedure is called the proper analysis here.

3. RESULTS AND DISCUSSION

3.1 Specific heat of copper

In order to determine the optimum heating rate of DSC, specific heat of copper with 99.99% in purity was measured with heating rates 1-20 K•min⁻¹ in the temperature range 290-360 K. The results at 350K were plotted as a function of heating rate in Fig.1. It shows the dependence of specific heat of copper on the heating rate of DSC. The heat capacity of sample with mass 33.86 mg was nearly equal with that of standard material, and symbol O in Fig.1 is the data processed with the proper analysis. Solid line was drawn by the least square method. These data depend linearly on the heating rate, and agree with recommended value [11] near at a heating rate 12 K•min⁻¹. Symbol ● indicates that the same output signals of symbol O were processed with unproper analysis in which the time lag of sample temperature was not considered. Deviation of these values are very large at lower heating rates than 12 K•min⁻¹, and are very small at higher heating rates. Figure 1 also shows that results obtained with heavy sample (solid triangle symbol) are in good agreement with recommended value, but in light sample (open triangle symbol), data were scattered. In considering with results obtained at other temperatures, the heating rate was determined to 10 K•min⁻¹ (0.167 K•s⁻¹) which is also the design value by manufacturer. Specific heat of copper measured at heating

rate 10 K•min⁻¹ agreed with recommended value less than 1.02 %, and data of two operators agreed within \pm 1 %.

3.2 Specific heats of water and synthetic sapphire

In order to check the reliability of the DSC, specific heats of water and synthetic sapphire were measured at heating rate 10 K•min⁻¹ under the condition of the equal heat capacities of sample and standard material.

Measured values of specific heat of distilled water agreed with recommended values [12] less than 3 % in the temperature range 300-340 K, and data of two operators agreed within 3 %. The uncertainty of the specific heat measurement of liquid was estimated to be± 3 %.

Agreement of measured value of specific heat of synthetic sapphire with the recommended value used in the analysis was less than 0.5 % in the temperature range 310-393 K.

3.3 Specific heat of water-based magnetic fluid

Many measurements with different sample mass were done. Figure 2 shows the variation of specific heat of water-based magnetic fluid as a function of sample mass. It is important that how to determine the unknown specific heat of magnetic fluid, because specific heat value obtained is 1.94 to 3.12 kJ· kg⁻¹· K⁻¹. The heat capacity measurement is optimized when DSC scans under the condition of that the heat capacity (specific heat times mass) of sample is equal to that of standard material. The heat capacity ratio was calculated and replotted in Fig.3. The specific heat of magnetic fluid with mass which heat capacity ratio nearly equals to one was adopted. Magnetic fluid with another magnetite concentration was also measured. Figure 4 shows the variation of specific heat of water-based magnetic fluid as a function of temperature. In this figure, specific heat shows weak temperature-dependence, but strong concentration-dependence. Figure 5 shows the variation of specific heat of magnetic fluid as a function of magnetite concentration. Solid line in Fig.5 is the

calculated value by the mixing rule of specific heat of mixtures. Specific heat data of water [12], magnetite [6] and oleic acid [6,7] were used. Measured and calculated values agreed within 6.7 %. The mixing rule of specific heat is useful for water-based magnetic fluid even when uncertainties of measurement, unknown surfactant, unknown specific heat of ultrafine magnetite particle and etc. are involved. Venger et al.[7] proved the validity of this rule for transformer oil-based magnetic fluid.

3.4 Specific heat of kerosene- based magnetic fluid

Figure 6 also shows the variation of specific heat of kerosene-based magnetic fluid as a function of temperature. Broken line in Fig.6 is the data of magnetic fluid measured by Venger et al.[7], and solid triangle symbol is the kerosene data measured by us. In Fig.7, variation of specific heat of kerosene-based magnetic fluid as a function of magnetite concentration shows the same tendency as in Fig.5. Solid line in Fig.7 is the calculated value by the mixing rule of specific heat using the measured data of kerosene. Measured and calculated values agreed within 6.5 %. The mixing rule of specific heat is also useful for kerosene-based magnetic fluid.

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FIGURE CAPTIONS

- Fig. 1. Specific heat of copper as a function of heating rate
- Fig. 2. Specific heat of water-based magnetic fluid as a function of sample mass
- Fig. 3. Heat capacity ratio of water-based magnetic fluid as a function of sample mass
- Fig. 4. Specific heat of water-based magnetic fluid as a function of temperature
- Fig. 5. Specific heat of water-based magnetic fluid as a function of magnetite concentration
- Fig. 6. Specific heat of kerosene-based magnetic fluid as a function of temperature
- Fig. 7. Specific heat of kerosene-based magnetic fluid as a function of magnetite concentration













